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STRUCTURE AND PHASE TRANSITIONS OF LIQUID CRYSTALS(U)  
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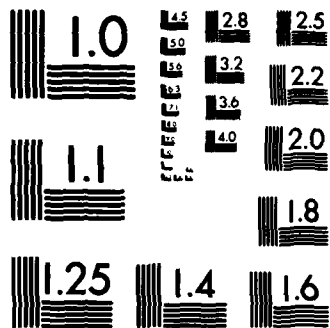
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Results of experimental and theoretical investigations of the structure and dynamic behavior of liquid crystals are summarized. Work performed includes studies of: switching dynamics of ferroelectric liquid crystals; the structure and phase transitions of liquid crystals of disc-shaped molecules; and of defects and macroscopic elastic effects in lamellar liquid crystals.		

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STRUCTURE, DYNAMICS AND PHASE TRANSITIONS OF LIQUID CRYSTALS

FINAL REPORT

NOEL A. CLARK

DECEMBER 27, 1982

U. S. ARMY RESEARCH OFFICE

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UNIVERSITY OF COLORADO

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## STRUCTURE AND PHASE TRANSITIONS OF LIQUID CRYSTALS

### I. SUMMARY OF RESULTS\*

#### A. Ferroelectric Liquid Crystals

Ferroelectric liquid crystals (FLCs) are attractive for electro-optic applications because the linear coupling of local molecular orientation to applied electric field,  $E$ , has two basic advantages over the typical quadratic dielectric coupling operative in nematics, both of which enhance response speed: stronger field induced torques at low  $E$ , and polarity which allows molecules to be driven in either direction by selecting the sign of  $E$ .

Our work to date shows that this SURFACE STABILIZED FERRO-ELECTRIC LIQUID CRYSTAL (SSFLC) geometry exhibits high speed (microsecond switching times), bistability (two stable states), response threshold, and large electro-optic response. These attributes make the SSFLC the most attractive liquid crystal mechanism for use in a variety of electro-optic applications from single element laser modulators to passive, matrix addressed array, graphic or pictorial displays. We have undertaken a research program aimed at understanding and developing SSFLC properties.

We have studied SSFLC switching dynamics, using optical microscopy with a pulsed nitrogen laser pumped dye laser light source to stroboscopically photograph various intermediate stages of switching with 20 nsec time resolution (9). This work has led us to formulate a model for the switching process (5). In order to understand the various switching structures and regimes in detail it is necessary to obtain static and dynamic solutions to the equation for the smectic C director orientation field  $\phi(r,t)$ . This

\* Numbered references refer to the publication list in Section II.



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nonlinear equation in its simplest form ( $K \nabla^2 \phi - P_0 E \sin \phi = \eta \partial \phi / \partial t$ ) subject to the nonlinear boundary condition ( $K \nabla \phi \cdot s - \Delta \gamma \sin 2\phi = 0$ ) has been solved analytically for a number of the simpler structures, including static linear domain walls and domain wall loops, surface unwinding of the ferroelectric helix, and domain wall motion at low applied fields (3),(14),(15).

A difficulty which must be addressed in both basic studies and device applications of SSFLCs is that the optimum liquid crystal layer thickness can often be very small, on the order of 1  $\mu\text{m}$ . Although uniform spacings of such dimensions can be readily achieved using optical flats, basic SSFLC studies require that such structures must be made out of thin glass to allow high resolution microscopy. Furthermore, for device applications they must be readily and inexpensively fabricated. An additional requirement is that the glass bounding plates be free to slide over each other for materials which require shearing for initial alignment of the smectic layers. To meet these requirements we have developed a distributed spacer technique, in which we use ordinary glass microscope slides or cover slips and determine the spacing between them with a photolithographically prepared array of  $\text{SiO}_2$  spacer pads, which can be made by evaporation down to controllable thicknesses of a few hundred Angstroms (15).

In collaboration with the organic chemistry group of Prof. D. Walba, Department of Chemistry, Univ. of Colorado, we have begun a small scale effort directed toward the synthesis of new ferroelectric liquid crystals. This effort has met with a significant initial success: a new family of chiral liquid crystals, several of which have ferroelectric phases near room temperature. Since directed synthesis requires a detailed knowledge of the relation of structure and phase behavior we have completed a comprehensive compilation of the molecular structures that give the smectic C phase (13).

## B. Liquid Crystals of Disc Shaped Molecules

We have developed the linear elastic-hydrodynamic theory of uniaxial columnar phases of disc-shaped molecules, in collaboration with Prof. J. Prost of the Bordeaux group. This theory is based on the general approach of the de Gennes and of Martin, Parodi, and Pershan and predicts a variety of novel effects including two anisotropic acoustic modes and permeation in two dimensions (1).

We have carried out a mean field calculation of the Isotropic - Nematic - Columnar phase diagram. This is an extension of Mc Millan's smectic A model to systems of disc-shaped molecules, and it predicts qualitatively similar behavior: a disc nematic phase appearing when the ratio of molecular radius to aromatic core radius decreases toward one. A notable difference is that the nematic-columnar transition is always first order in this model (4).

We have discovered that columnar liquid crystals of disc-shaped molecules can be drawn into thin (diameter  $\approx 1 \mu\text{m}$ ) elongated strands, freely suspended in air, in which the columns run parallel to the strand axis. Of particular interest are strands of tilted columnar phases in which the molecular director (the average disc normal) is tilted with respect to the strand (z) axis. These strands are characterized by  $\phi(z,t)$ , the local orientation of  $n$  about the strand axis. In this regard they represent a physical realization of a one dimensional nematic, i.e. the field  $\phi$  has Frank-like elasticity. An additional feature of  $\phi(z,t)$  is the occurrence of orientational kinks where  $n$  hops from one stable orientation relative to the column lattice to another (8).

### C. Lamellar Liquid Crystals

We have demonstrated that it is possible to use elastic light scattering to obtain quantitative information on the structure, dimensions, and arrangement of smectic A focal conic defects. Parabolic focal conic (PFC) arrays, generated by dilation of smectic A samples, were shown to give rise to a characteristic light scattering pattern, analysis of which provided the focal length,  $f$ , of the parabolic line defects. We were able to prove the existence of PFC defects with focal lengths as small as one smectic layer thickness, suggesting that this is the minimum focal length possible. Since PFC defects with  $f$  this small are not detectable by microscopy, this work shows that light scattering can provide otherwise unattainable quantitative information about focal conic defects (6).

Biological membrane fragments, whether natural or artificial, are sheet-like structures which, if they are ordered into multilamellar arrays, can be effectively studied by various biophysical techniques (xray diffraction, dichroic and Raman spectroscopy, NMR, etc.) These multilayer arrays, in which the sheets are planar and equally spaced, have the smectic A liquid crystal structure. In collaboration with K. Rothschild we have analyzed theoretically the formation and structure of smectic A multilamellar arrays made from finite sized membrane fragments (8). These considerations have led to the design of a new process for the production of multilamellar arrays: Isopotential Spin Dry Centrifugation, in which arrays are compacted while spinning at high  $g$  by dehydration onto a gravitational isopotential surface. This method has produced the best aligned arrays of natural membrane fragments yet available. In collaboration with K. Rothschild and S. Gruner, we have made a detailed freeze fracture and xray diffraction study of the structure of arrays made from of bovine retinal rod outer segment disc membranes (10).



## II. PUBLICATIONS

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- (2) "CHIRALLY ASYMMETRIC REVERSIBLE PHOTOBLEACHING IN PURPLE MEMBRANE FILMS", N. A. Clark and K. J. Rothschild, *Biophysical Journal* 33, 217a (1981).
- (3) "DOMAIN WALLS IN FERROELECTRIC SMECTIC C CRYSTALS", M. Handschy and N. A. Clark, *Bulletin of the American Physical Society* 26, 275 (1981).
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- (6) "ELASTIC LIGHT SCATTERING BY SMECTIC A FOCAL CONIC DEFECTS", N. A. Clark and A. J. Hurd, *Journal de Physique* 43, 1159-1165 (1982).
- (7) "FREELY SUSPENDED STRANDS OF TILTED COLUMNAR LIQUID CRYSTAL PHASES: ONE DIMENSIONAL NEMATICS WITH ORIENTATIONAL JUMPS", D. H. Van Winkle and N. A. Clark, *Physical Review Letters* 48, 1407-1410 (1982).
- (8) "PREPARATION OF ORIENTED MULTILAMELLAR ARRAYS OF NATURAL AND ARTIFICIAL BIOLOGICAL MEMBRANES", N. A. Clark and K. J. Rothschild in *Methods in Enzymology*, L. Packer, Ed., Academic Press, New York (1982) pp. 326-333.
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- (12) "FERROELECTROHYDRODYNAMIC INSTABILITIES IN CHIRAL SMECTIC C LIQUID CRYSTALS", N. A. Clark and P. Young, *Applied Physics Letters* (submitted).
- (13) "THE LIQUID CRYSTAL SMECTIC C PHASE", S. T. Lagerwall, N. A. Clark, B. Stebler, M. Nilsson, and B. Otterholm (submitted to *Molecular Crystals and Liquid Crystals*).

- (14) "ELECTRO-OPTIC EFFECTS IN FERROELECTRIC LIQUID CRYSTALS", N. A. Clark, M. A. Handschy, and S. T. Lagerwall (to appear in Molecular Crystals and Liquid Crystals, 1983).
- (15) "SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTAL STRUCTURES EXHIBITING NON-UNIFORM DIRECTOR AND POLARIZATION ORIENTATION", M. A. Handschy and N. A. Clark, Bulletin of the American Physical Society, March, 1983.

### III. SCIENTIFIC PERSONNEL SUPPORTED

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D. H. Van Winkle - M. S., Research topic: Freely Suspended Liquid Crystal  
Strands.

W. Thurmes - Research topic: Synthesis of Ferroelectric Liquid Crystals.

J. Morrison - Research topic: Surface Effects in Liquid Crystals.

D. Bass - Research topic: Multilamellar Arrays of Biological Membranes.

T. Rieker - Microfabrication of ferroelectric liquid crystal devices.

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